END
DATE
FILMED

79
DDC

067540

LEVEL

C78-1232/501

Charge Transport in Oxidation Product of

Lutetium Diphthalocyanine

by

M. M. Nicholson and F. A. Pizzarello

Prepared for Publication

in the

Journal of the Electrochemical Society

D D C

APR 10 1979

C

Electronics Research Center
Rockwell International
Anaheim, California

October 31, 1978

79 04 09 106

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
CHARGE TRANSPORT IN OXIDATION PRODUCT OF LUTETIUM DIPHTHALOCYANINE.	Technical rept. no. 1 Sep 77 – 31 Aug 78
	6. PERFORMING ORG. REPORT NUMBER C78-1232/501

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
M. M. Nicholson and F. A. Pizzarello	N00014-77-C-0636

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Electronics Research Center Rockwell International 3370 Miraloma Avenue, Anaheim, CA. 92803	34 p.

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research 800 N. Quincy Arlington, VA. 22217	31 October 1978
	13. NUMBER OF PAGES 32

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

This document has been approved for public release and sale; its distribution is unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Diphthalocyanines
Charge transport
Electrochromism

4 BY TEN TO THE MINUS 6TH POWER SQ CM

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A red/green anodic-reaction boundary was propagated in a lutetium diphthalocyanine film by application of a constant current through a metallic and an electrolytic contact. From the boundary velocity and the electric field in the red phase, the oxidation product was found to contain a charge carrier with a concentration approximately twice that of the dye molecules and a mobility of 4×10^{-6} cm^2/V-sec. These results and the charge compensation requirement of the boundary process suggested that the red oxidation product

was a solid anion conductor.   The estimated bulk resistivity of the red
material at room temperature was 1600 ohm-cm.

ACCESSION for

NTIS	White Section
DDC	Buff Section ☐
UNANNOUNC'D	☐
JUSTIFICATION	☐

BY

DISTRIBUTION/AVAILABILITY CODES

| Dist | | SPECIAL |
| A | | |

CHARGE TRANSPORT IN OXIDATION PRODUCT OF LUTETIUM DIPHTHALOCYANINE

M. M. Nicholson* and F. A. Pizzarello

Electronics Research Center, Rockwell International, Anaheim, California 92803

ABSTRACT

A red/green anodic-reaction boundary was propagated in a lutetium diphthalocyanine film by application of a constant current through a metallic and an electrolytic contact. From the boundary velocity and the electric field in the red phase, the oxidation product was found to contain a charge carrier with a concentration approximately twice that of the dye molecules and a mobility of 4×10^{-6} cm^2/V-sec. These results and the charge compensation requirement of the boundary process suggested that the red oxidation product was a solid anion conductor. The estimated bulk resistivity of the red material at room temperature was 1600 ohm-cm.

The lanthanide elements form diphthalocyanines with the proposed molecular structure shown in Fig. 1. When the metal is tri-valent, one labile hydrogen remains in the complex. Hence, the formula may be abbreviated $MH(Pc)_2$, where M denotes a lanthanide ion and Pc represents the divalent group $C_{32}H_{16}N_8^{-2}$. Soviet investigators have published a number of papers on this series of compounds since 1965 (1-9)*. The electrochemistry is unusual. Moskalev and Kirin found that the absorption spectrum of a lutetium diphthalocyanine film on a tin oxide electrode in aqueous potassium chloride underwent major, essentially rever-sible, changes as the applied potential was varied from -0.8 to 1.0 V vs Ag/AgCl (3,6). Different mechanisms were proposed for the changes at cathodic and anodic potentials. The film was initially green. A shift toward blue-green at negative poten-tials was attributed to field-induced ionization of the solid dye material, and a "cinnamon" color, produced anodically, was thought due to complexing with oxygen or water. Although these steps may be involved, they do not fully account for the re-sponses of this system observed subsequently in our laboratory (10,11).

We found deep blue and violet forms at more negative potentials and several shades of red in the positive region. Preliminary charge-density measurements indicated the

---

*Only a partial bibliography is given.

2

occurrence of at least one cathodic and one anodic faradaic process (10). The reactions were surprisingly fast at film thicknesses of about 50 molecular layers. All color changes occurred in less than 50 msec under potentiostatic pulses, even though the reactants and products remained on the electrode as an insoluble film. The color variety and fast responses persisted at -50° in a 30 wt % $CaCl_2$ electrolyte. Because of this behavior, the rare-earth diphthalocyanines are of special interest for electrochromic display applications (10,11).

The fast electrode kinetics led us to postulate solid-state conduction in all color states of the dye material; a non-conductive product formed at any stage would tend to block the reaction. Neodymium diphthalocyanine was already known to be an electronic semiconductor with a bulk resistivity of 23 ohm-cm at 25° in pressed-powder form (2). This paper reports an investigation of charge transport in the red oxidation product of lutetium diphthalocyanine by a solid-state moving-boundary technique. The carrier concentration and mobility were evaluated on the basis of a one-carrier model. Although the mobile species has not yet been identified, the results suggest that the red material is a solid anion conductor with a room-temperature resistivity of 1600 ohm-cm.

3

Experimental

Lutetium diphthalocyanine was synthesized from lutetium acetate and o-phthalonitrile by the method of Moskalev and Kirin (4). The dye films were prepared by vacuum sublimation from a small heated source onto a stationary alumina substrate at $\sim 10^{-5}$ torr. Details of the synthesis and film deposition procedures are given in Reference 10. The color density of the film provided a visual estimate of its thickness during evaporation. The dye concentration in the finished film was determined from its optical density (OD) at the 668-nm absorption peak, measured on a Perkin Elmer Model 202 dual-beam spectrometer. It was established previously (10) that the film concentration in molecules/cm^2 was given by $c_0 = 7.25 \times 10^{15} \times$ (OD). The optical density ranged from 0.4 to 1.2 in the present work.

For investigation of transport processes in the dye material, the films were deposited on an insulator instead of tin oxide. The substrates were laser-cut strips of single-crystal Czochralski-grown sapphire, 1.25 cm wide and approximately 4.5 cm long. The (01$\bar{1}$2) crystallographic plane was exposed to the dye, and the long edges of the strips were oriented in the [$\bar{2}$021] direction. A gold contact 4 mm wide was sputtered across one end of the specimen, on top of the dye. The other end dipped into an air-

4

saturated aqueous electrolyte, either 1 M KCl or 1 M Na_2SO_4.

The cell arrangement and instrumentation are indicated in Fig. 2. The dye specimen on the sapphire strip was attached to an interior wall of a Klett colorimeter cell with a small amount of soft wax. The counter and reference electrodes were Ag/AgCl in the KCl electrolyte and $Pb/PbSO_4$ in the Na_2SO_4. Agar salt bridges were used to separate these electrodes from the main cell compartment in the sulfate solution. A constant anodic current was supplied by a Princeton Applied Research 173 galvanostat, and the total voltage between the reference and test electrodes was monitored with a Keithley 610C electrometer and strip chart recorder.

Before the experiment began, a line was engraved across the lower end of the specimen with a diamond scriber. Electrolyte was added to the cell until the level was approximately 1 mm above the scribe line. This line defined the lower end of the electrical path in the film. It also acted to nucleate a uniform boundary in the potassium chloride solution. The color change began at the liquid level instead of the scribe line in sodium sulfate.

For observation of the moving red/green boundary, the cell was inserted in a commercial table-top color-slide viewer, which provided back illumination and approximately 2X magnification. A piece of millimeter graph paper was taped on the back of the

5

Klett cell to locate the boundary position. The propagation
distance of the red region was determined at frequent intervals,
either by direct reading or by counting the number of red milli-
meter squares and dividing by the film width. The latter method,
yielding an average distance, was preferred in the case of a
slightly irregular boundary.

The voltage distribution in the red film was of primary
interest. Since small electrolytic or electronic probes could
not be attached to the film with the cell arrangement used, an
"electrolyte probe" technique was devised. After the boundary
had advanced about 10 mm, the electrolyte level was raised in
successive increments of $\sim$ 1 mm, with the current still applied.
This effectively shorted the portion of the red film below the
liquid surface, and a corresponding abrupt drop in the total
voltage occurred. Meanwhile, the green-film resistance was
unchanged. The voltage distribution throughout the red region
was determined in this way.

6

Results and Discussion

Observations.--Under constant anodic current, the red color was propagated upward from the liquid electrolyte. The red/green boundary was quite sharp, and the region below it had a uniform red color. The transport properties reported herein are for this red film, unwetted by the electrolyte.

Experimentally, both the boundary velocity and the electric field in the red phase were found to be constant for a given applied current. These simple results made it possible to calculate a carrier concentration and mobility for the red material. Sheet resistivities of the red and green films were also found, and bulk resistivities were estimated from those values and the apparent film thickness based on the initial optical density.

In Fig. 3 and 4, propagation distances for the KCl and Na_2SO_4 electrolytes are shown as functions of time at several constant currents. The points fell on straight lines passing through the origin, with slopes essentially proportional to the current density. Hence, for a given film the coloring process required a constant number of charges per unit area, or per molecule of dye.

Figures 5(a) and 6(a) show total voltage measured during boundary propagation. In a typical experiment, that voltage

7

increased linearly with both time and propagation distance for
an extended period. Eventually, it tended to rise more rapidly,
although the distance-time function remained linear. Some
results obtained with the electrolyte-probe technique are
shown in Fig. 5(b) and 6(b).

Transport Model.--One-dimensional transport of a charged species
i in an electric field is governed by Eq. 1

$$\frac{\partial c_i}{\partial t} = D_i \quad \frac{\partial}{\partial x} \left[\frac{\partial c_i}{\partial x} + \frac{zF}{RT} c_i \frac{\partial E}{\partial x} \right] \qquad [1]$$

where c_i is the concentration of the mobile species with charge
z, and D_i is its diffusion coefficient; t is time, x is distance,
E is potential, and the term F/RT has its usual meaning (12). In a
multi-carrier system, the different mobile species generate a
set of simultaneous equations in this form, and the treatment
can be complicated. However, many solids conduct predominantly
by one mobile species with a transference number near unity.
A single equation as in [1] then suffices. The transport data
for the red dye material were analyzed on the basis of a one-
carrier model.

Although the color boundary continued to advance, the red
region behind it was in a steady state, indicated by constancy
of the boundary velocity at constant applied current. Then

8

$\partial c_i/\partial t$ was zero, and Eq. [1] could be integrated to obtain an expression for the carrier flux f_i.

$$f_i = D_i \frac{\partial c_i}{\partial x} + D_i \frac{zF}{RT} c_i \frac{\partial E}{\partial x} \qquad [2]$$

The first term on the right side of Eq. [2] is the diffusion flux, and the second term is the flux due to migration in the electric field.

It is easily deduced that the diffusion term was negligible in the moving-boundary experiments: With constant current density, the total flux was constant. Under steady-state conditions, the concentration gradient also was constant in time, though not necessarily zero at any point in space. It was found experimentally, however, that the electric field was constant in time and independent of distance. With constant values of f_i, $\partial c_i/\partial x$, and $\partial E/\partial x$ in both time and space, it is evident from Eq. [2] that c_i must have been constant. Then $\partial c_i/\partial x = 0$, and the diffusion flux was zero.

The carrier mobility then could be calculated from the electric field $\mathcal{E}$ and the carrier velocity $\partial x/\partial t$, which was the same as the velocity of the boundary:

$$\mu_i = \frac{1}{\mathcal{E}} \frac{\partial x}{\partial t} \qquad\qquad (\mathcal{E} \equiv \frac{\partial E}{\partial x}) \qquad [3]$$

9

The product zc_i was related to the current density I and the velocity through Eq. [4]

$$I = \frac{i}{w\delta} = zc_i F\frac{\partial x}{\partial t} \tag{4}$$

where c_i is the bulk concentration, i is the total current, w is the width of the film, and δ is its thickness. Since δ was not accurately known, it was appropriate to use a surface or film concentration $c_{i(s)}$, which may be expressed in moles per unit area.

$$c_{i(s)} = \delta c_i \tag{5}$$

Then, from Eq. [4],

$$zc_{i(s)} = \frac{i}{wF(\partial x/\partial t)} \tag{6}$$

Evaluation of Resistivities.--The total voltage measured with respect to the reference electrode was the sum of three boundary potentials and an ohmic term:

$$E_{total} = E_s + E_b + E_m + i(R_r + R_g) \tag{7}$$

In Eq. [7], E_s is the potential difference at the red film/ solution interface, E_b is the potential difference at the red/green boundary, E_m is the potential difference at the green film/metal boundary,

10

and R_r and R_g are the total resistances of the red and green sections. Although the interfacial potentials were not individually known, they should have remained constant at a given current density, once the propagation was established. The film resistances were related to the sheet resistivities $\rho_{r(s)}$ and $\rho_{g(s)}$ (ohms/square) through Eq. [8]

$$R_r + R_g = [\rho_{r(s)} - \rho_{g(s)}] (x/w) + \rho_{g(s)} \ell/w \qquad [8]$$

where ℓ represents the total length of the film specimen. The resistivities are treated here as constants independent of distance within the respective phases. From Eq. [7] and [8], it is evident that

$$\partial E_{total}/\partial x = (i/w)[\rho_{r(s)} - \rho_{g(s)}] \qquad [9]$$

Hence, the difference in sheet resistivities was obtained from the slope of a plot of E_{total} vs x, as in Fig. 5(a) and 6(a). The sheet resistivity of the red film was determined separately by the electrolyte probe technique. Since this was a relatively fast procedure, R_g remained constant. Hence, $\rho_{r(s)}$ could be found from a plot of the type in Fig. 5(b) and 6(b).

$$\rho_{r(s)} = \frac{\partial E}{\partial x} \frac{w}{i} \qquad (R_g = constant) \qquad [10]$$

11

Table 1 gives the measured sheet resistivities of the red and green films and the corresponding bulk resistivities calculated from film thicknesses based on the approximate crystal density of 1.58 g/cm^3 for $LuH(Pc)_2$. This density was estimated from that of $U(Pc)_2$ (13), with the assumption that the two compounds have the same crystal structure and unit-cell dimensions. The average bulk resistivity of the red product was 1300 ohm-cm in the KCl experiments and 2000 ohm-cm in the Na_2SO_4. In all cases, the red film was more resistive than the green, which is an electronic conductor (2). The variations in bulk resistivities observed among the different specimens were not surprising, since the film-deposition process was not precisely controlled.

Interpretations.--Table 2 summarizes results of the transport experiments. Although the applied currents were at the micro-ampere level, the estimated current densities through the cross sections of the films ranged from 15 to 150 mA/cm^2, as noted in Table 1. The carrier concentration term $zc_{i(s)}$, from Eq. [6], was approximately twice the concentration c_o of the dye molecules. This carrier concentration is unusually high for an organic solid without metallic character. It was not sur-prising to find that the color conversion may occur by a 2-electron faradaic process. A reaction product containing two units of

12

mobile charge per molecule was not anticipated, however. The small integral ratio of carriers to dye molecules strongly suggests that the red material is an ionic conductor with one divalent or two monovalent mobile ions per molecular unit.

The mobility calculated from Eq. [3] was of the order of 4×10^{-6} cm^2/V-sec. This magnitude is more typical of an ion in a stoichiometric solid electrolyte than of an electronic charge carrier. It is comparable to 8×10^{-6} cm^2/V-sec for H^+ in polycrystalline hydrogen uranyl phosphate (14) and 1.2×10^{-5} cm^2/V-sec for Ag^+ in single-crystal silver beta alumina (15), both at 25°. The concept of mobile ions in lutetium diphthalocyanine is consistent with the open crystal structures of $Th(Pc)_2$ and $U(Pc)_2$ (7,13).

Ionic conduction is also quite acceptable in terms of reaction mechanisms. Electrons are removed from the dye molecules at the color boundary and transported through the green film to the external circuit. The red oxidation product is a neutral material with a different chemical composition. These conditions require a compensation process involving both charge and material transport in the red phase. Such compensation could occur by loss of cations or gain of anions at the solution boundary.

Since $LuH(Pc)_2$ should contain one labile hydrogen, proton loss with formation of Lu(IV) may be considered:

$$LuH(Pc)_2 \rightarrow Lu(Pc)_2 + H^+ + e^- \qquad\qquad [I]$$
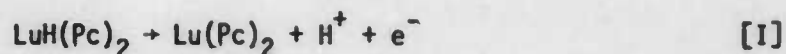
This reaction would correspond to $n = 1$, however, and the moving-boundary experiments yielded n values closer to 2. Moreover, the product $Lu(Pc)_2$ provides no obvious path for continuing transport of protons from their source at the reaction boundary, through the red film, to the electrolyte solution. If such transport did occur, the boundary velocity should decrease with propagation distance; this was not observed. Hence, the cation mechanism seems improbable.

The anion mechanism can be represented by

$$LuH(Pc)_2 + yA^{-Z} \rightarrow LuH(Pc)_2 \cdot yA + ne^- \quad (n = yz) \qquad [II]$$
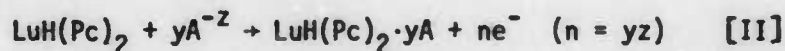
The product would consist of the mobile anions A^{-Z} in an immobile organic cation lattice. With a chloride electrolyte, the reaction could be

$$LuH(Pc)_2 + 2Cl^- \rightarrow LuH(Pc)_2 \cdot 2Cl + 2e^- \qquad\qquad [III]$$
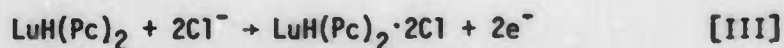
Anodic formation of a halogen complex is consistent with results of tracer studies by Moskalev and Kirina, which showed that a lutetium diphthalocyanine anode can remove traces of iodine, originally present as $I,^-$ from a supporting electrolyte

14

solution (9). The anion A^{-z} in the case of the sulfate solution might be OH^-, or possibly HO_2^- or $SO_4^=$.

The mobility measurements were not precise enough to distinguish between the different anions in the red film. However, the average experimental n was 2.5 for the chloride electrolyte and 1.8 for the sulfate; it is possible that the n values actually are different for the faradaic reactions in the two electrolytes. Experimental deviation from an integral value of n could be due to several factors, including electrolytic side reactions and some inaccuracy in determining the surface concentration of the dye (10).

Transport properties of the rare-earth diphthalocyanines are important in electrochromic display applications. Faughnan, Crandall, and Lampert found, for example, that a space-charge-limited proton current controlled the bleaching rate in the tungsten oxide electrochromic system (16). The calculated proton mobility in the blue cathodically formed tungsten bronze was 8×10^{-7} cm^2/V-sec. The mobilities reported here for the charge carrier in oxidized lutetium diphthalocyanine are about five times larger. This factor must contribute to its faster electrochromic response. Investigations of electrode reactions and transport mechanisms in the diphthalocyanines are continuing.

15

Acknowledgments

SYMBOLS

c_i	concentration of species i, moles/cm^3
$c_{i(s)}$	surface concentration of species i, moles/cm^2 or molecules/cm^2
c_o	surface concentration of dye, molecules/cm^2
D_i	diffusion coefficient of species i, cm^2/sec
E	electrical potential, volts
E_b	potential difference at reaction boundary, volts
E_m	potential difference at green film/metal interface, volts
E_s	potential difference at red film/solution interface, volts
E_{total}	potential difference between metal contact and reference electrode, volts
$\mathcal{E}$	electric field in red film, V/cm
F	faraday constant, 96,494 C/g-equiv
f_i	flux of species i, moles/cm^2-sec
I	current density, A/cm^2 or mA/cm^2
i	total current, A or μA
ℓ	total length of film specimen, cm
n	electrons lost per molecule of dye in color conversion process
OD	optical density
R	gas constant, 8.314 joules/deg-mole
R_g	total resistance in green film, ohms
R_r	total resistance in red film, ohms

17

T	absolute temperature, °K
t	time, sec or min
w	width of film specimen, cm
x	distance, cm
y	anions utilized per molecule of dye in color conversion process
z	number of charges on species i
δ	thickness of dye film, cm
μ_i	mobility of species i, cm^2/V-sec
ρ_g	bulk resistivity of green dye, ohm-cm
ρ_r	bulk resistivity of red dye, ohm-cm
$\rho_{g(s)}$	sheet resistivity of green dye, ohms/square
$\rho_{r(s)}$	sheet resistivity of red dye, ohms/square

REFERENCES

1. I. S. Kirin, P. N. Moskalev, and Yu. A. Makashev, Russ. J. Inorg. Chem., 10, 1065 (1965).

2. I. S. Kirin and P. N. Moskalev, Russ. J. Phys. Chem., 41, 251 (1967).

3. P. N. Moskalev and I. S. Kirin, Optics and Spectrosc., 29, 220 (1970).

4. P. N. Moskalev and I. S. Kirin, Russ. J. Inorg. Chem., 15, 7(1970).

5. I. S. Kirin and P. N. Moskalev, Russ. J. Inorg. Chem., 16, 1687 (1971).

6. P. N. Moskalev and I. S. Kirin, Russ. J. Phys. Chem., 46, 1019 (1972).

7. I. S. Kirin, A. B. Kolyadin, and A. A. Lychev, J. Struct. Chem. (USSR), 15, 415 (1974).

8. P. N. Moskalev and N. I. Alimova, Russ. J. Inorg. Chem., 20, 1474 (1975).

9. P. N. Moskalev and N. I. Kirina, J. Appl. Chem. (USSR), 48, 370 (1975).

10. M. M. Nicholson and R. V. Galiardi, Final Report, Contract N62269-76-C-0574, AD-A039596, May 1977; Chem. Abstr. 87: 144073v.

11. M. M. Nicholson and R. V. Galiardi, SID International Symposium Digest, IX, 24 (1978).

12. P. Delahay, Ch 5 in P. Delahay and C. W. Tobias, Ed., "Advances in Electrochemistry and Electrochemical Engineering," Vol. 1, Wiley-Interscience, New York, 1961.

13. A. Gieren and W. Hoppe, J. Chem. Soc. (London), Sec. D, Chem. Comm., 413 (1971).

14. P. E. Childs and T. K. Halstead, Mat. Res. Bull., 13, 609 (1978).

15. M. S. Whittingham and R. A. Huggins, This Journal, 118, 1 (1971).

16. B. W. Faughnan, R. S. Crandall, and M. A. Lampert, Appl. Phys. Lett., 27, 275 (1975).

Table 1. Film Resistivities of Lutetium Diphthalocyanine and Its Red Oxidation Product*

Specimen	Initial OD At 670 nm	Current Density** (mA/cm²)	$\rho_g(s)$ (ohms/square) x 10-8	$\rho_r(s)$ (ohms/square) x 10-8	ρ_g (ohm-cm) x 10-3	ρ_r (ohm-cm) x 10-3
1 M KCl Electrolyte+						
1	0.48	14	1.3	1.8	0.52	0.72
		37	0.2	1.4	0.09	1.3
		145	0.93	4.2	0.41	2.1
2	0.88	50	0.56	1.1	0.45	0.91
					Avg 0.37	Avg 1.3
1 M Na₂SO₄ Electrolyte+						
4	0.89	50	0.68	1.1	0.55	0.88
5	1.00	87	0.24	0.69	0.22	0.63
6	1.20	22	2.1	4.0	2.3	4.4
		37	--	2.6	--	2.9
		73	0.78	1.2	0.86	1.3
					Avg 0.98	Avg 2.0
Two Gold Contacts Without Electrolyte						
8	0.89	10	1.3	--	1.1	--

*Green-film conduction is electronic; red-film conduction probably is ionic.
**Based on film thickness estimated from crystal density.
+Air-saturated.

Table 2. Charge Transport Properties in Oxidation Product of Lutetium Diphthalocyanine

Specimen*	Current (A) $\times 10^7$	$\partial x/\partial t$ (cm/sec) $\times 10^4$	$\mathcal{E}$ (V/cm)	$zc_i(s)$ (molecules/cm^2) $\times 10^{-16}$	n $(zc_i(s)/c_0)$	μ_i (cm^2/V-sec) $\times 10^6$
			1 M KCl Electrolyte**			
1	1 2 8	0.55 1.00 4.5	14 23 300	0.91 1.00 0.89	2.6 2.8 2.6	3.9 4.3 1.9
2	5	2.5	45	1.28	2.0	5.9
3*	3	0.83	--	1.81	2.3	--
					Avg 2.5	Avg 4.0
			1 M Na$_2$SO$_4$ Electrolyte**			
4	5 5	3.3 2.9	43 85	0.75 0.87	1.2 1.3	6.6 3.3
5	10	3.7	55	1.36	1.9	6.6
6	2 3 5 10	0.63 0.87 1.53 3.65	-- 96 104 95	1.60 1.70 1.60 1.30	1.8 1.9 1.8 1.5	-- 3.8 1.5 0.9
7*	1	0.160	--	3.10	3.4	--
					Avg 1.8	Avg 4.3

*OD was 1.20 for Specimen 3 and 1.24 for Specimen 7; given for others in Table 1. Specimen width w was 1.25 cm in all cases.
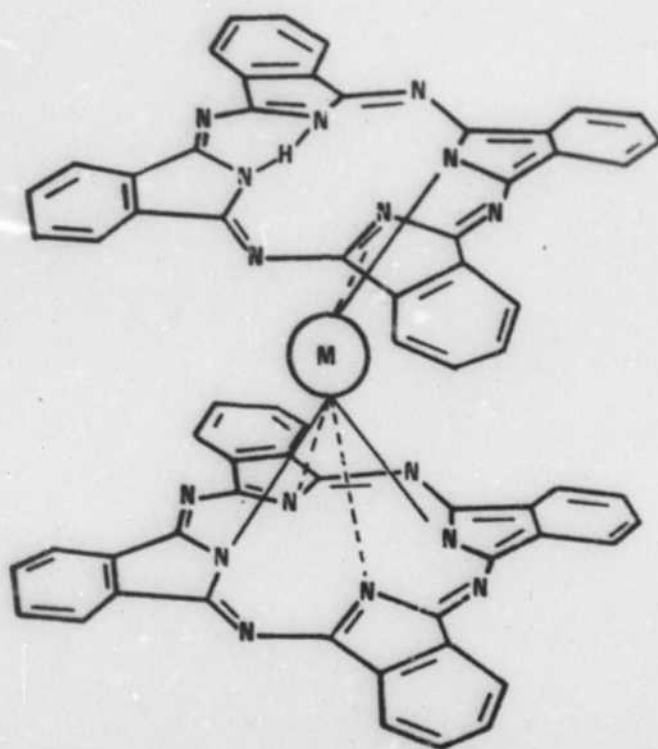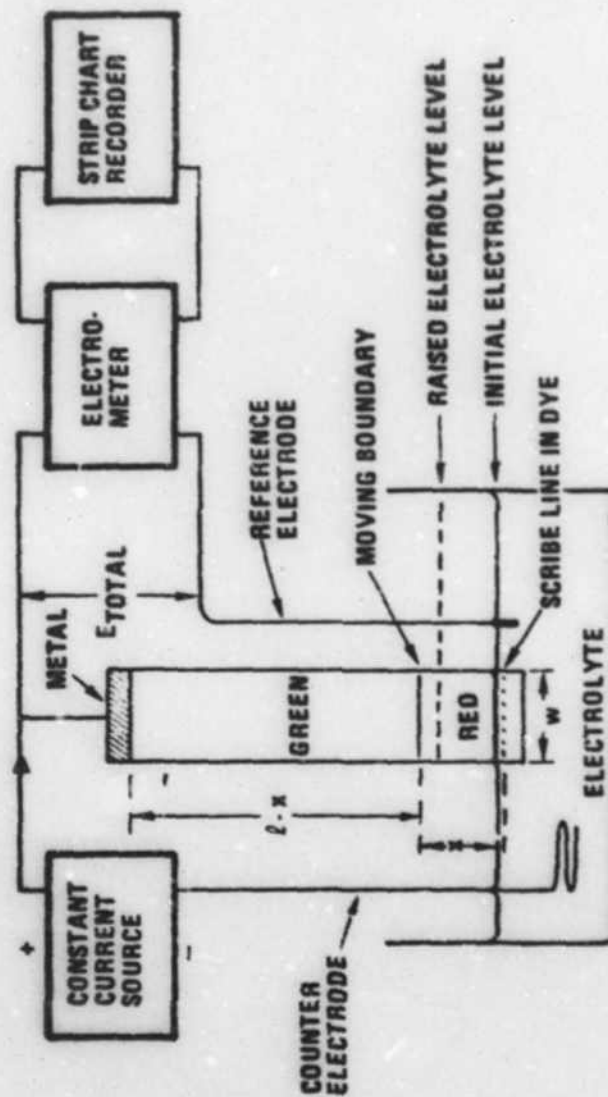**Air-saturated.

Illustrations

Fig. 1

Fig. 2

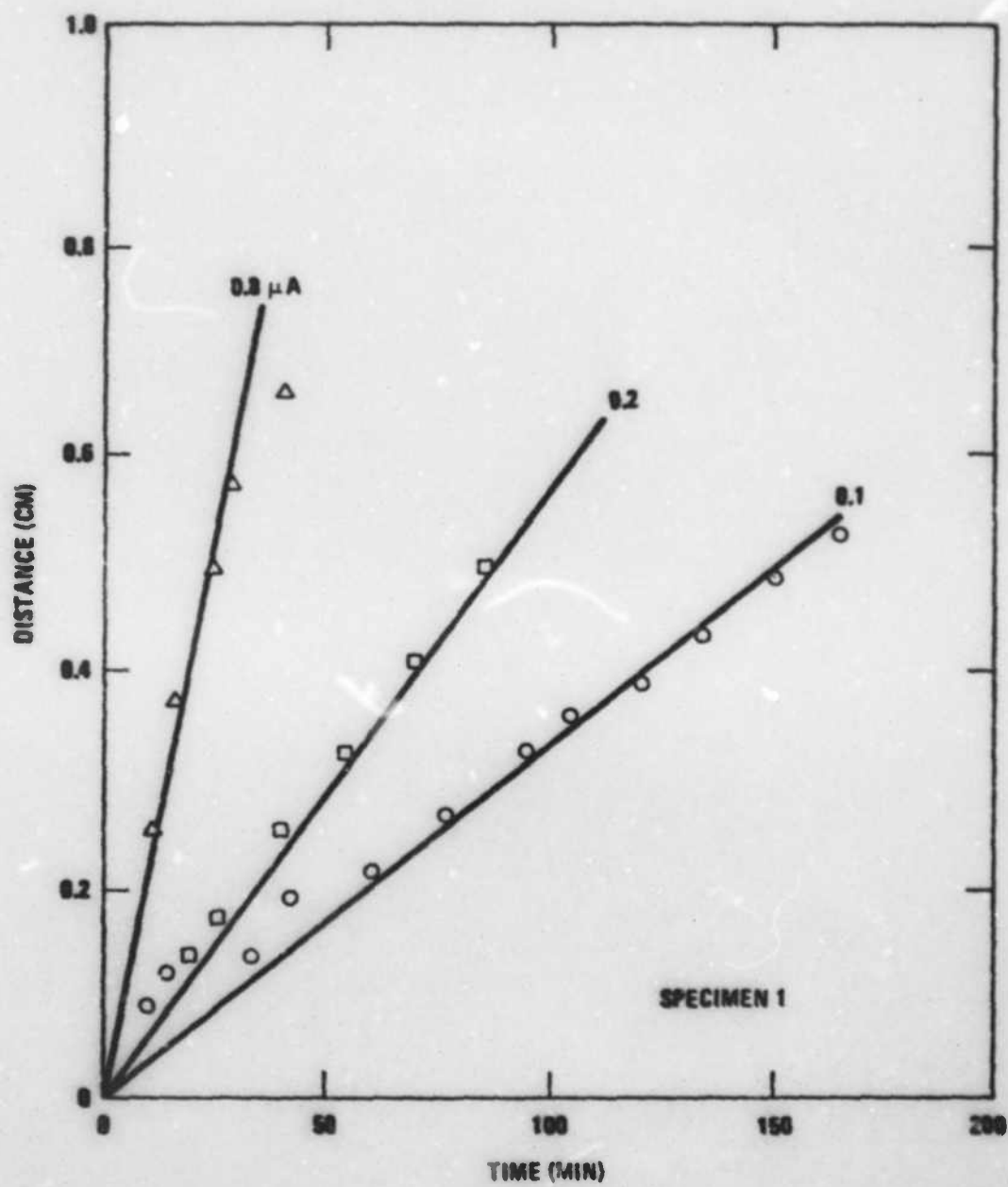Fig. 3

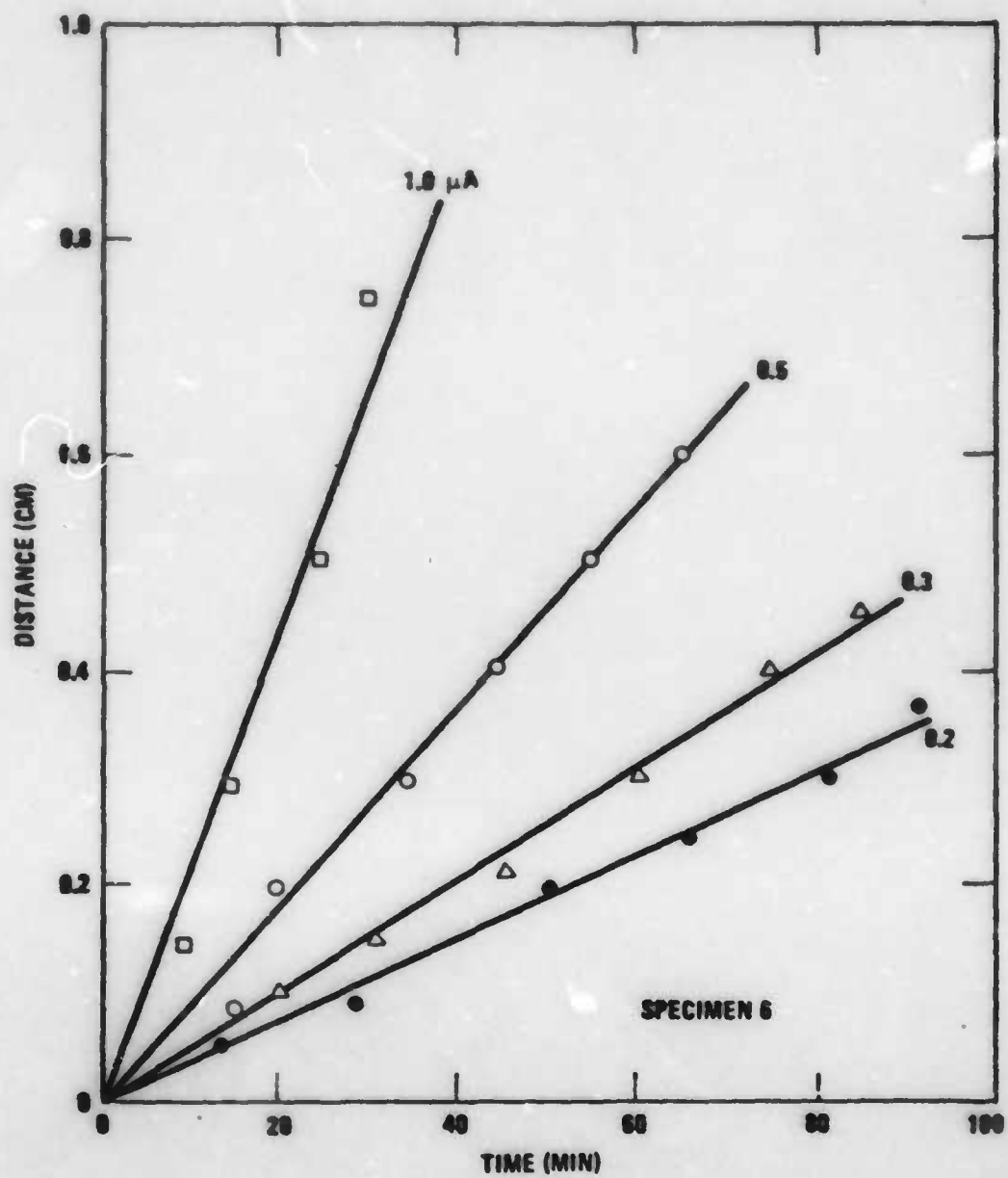Fig. 4

Fig. 5

Fig. 6

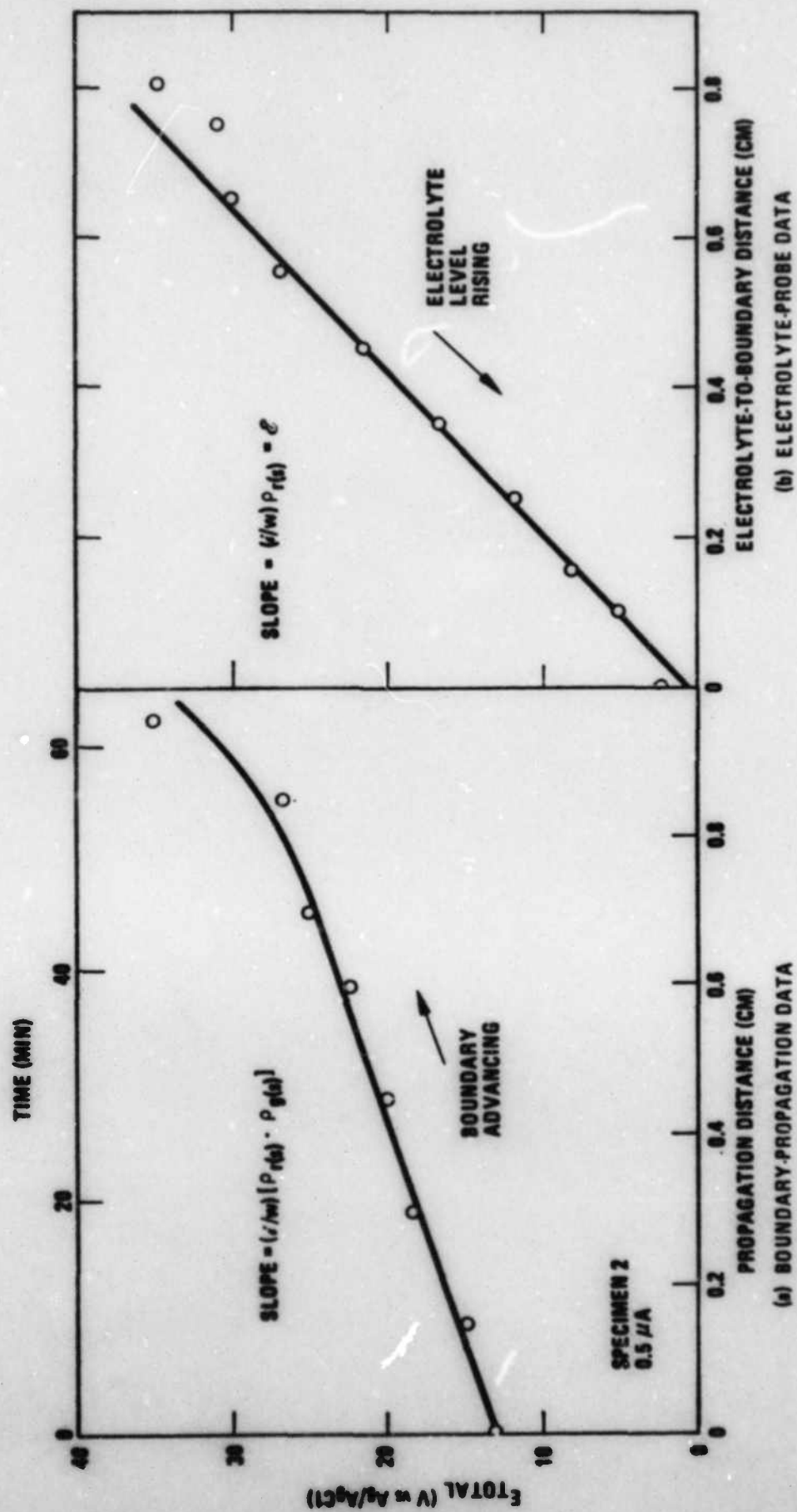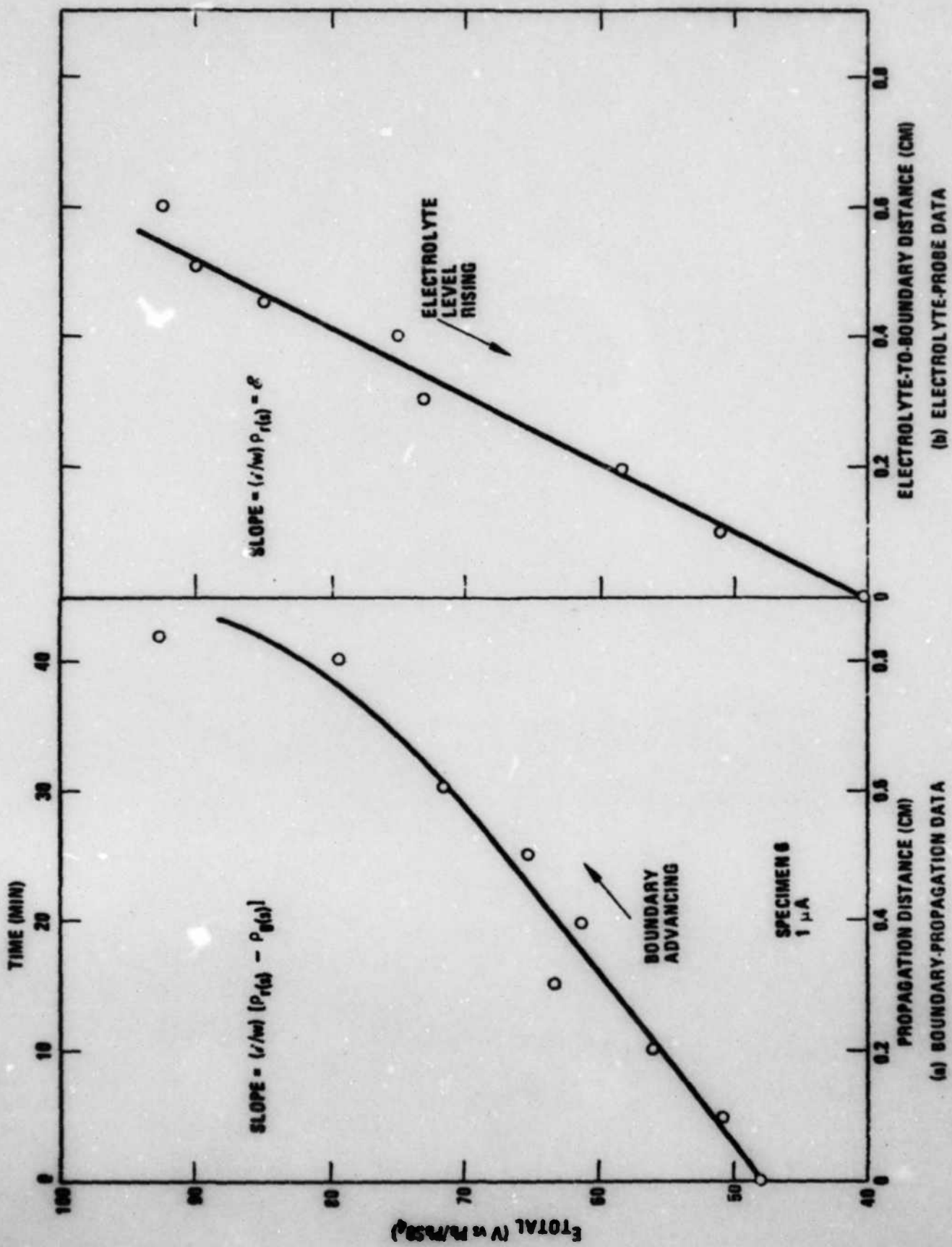## TECHNICAL REPORT DISTRIBUTION LIST, 359

<table>
<tr><td></td><td>No.
Copies</td></tr>
<tr><td>Dr. H. Richtol
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181</td><td>1</td></tr>
<tr><td>Dr. A. B. Ellis
Chemistry Department
University of Wisconsin
Madison, Wisconsin 53706</td><td>1</td></tr>
<tr><td>Dr. M. Wrighton
Chemistry Department
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139</td><td>1</td></tr>
<tr><td>Larry E. Plew
Naval Weapons Support Center
Code 3073, Building 2906
Crane, Indiana 47522</td><td>1</td></tr>
<tr><td>S. Ruby
DOE (STOR)
600 E Street
Washington, D.C. 20545</td><td>1</td></tr>
<tr><td>Dr. Aaron Wold
Brown University
Department of Chemistry
Providence, Rhode Island 02192</td><td>1</td></tr>
<tr><td>Dr. R. C. Chudacek
McGraw-Edison Company
Edison Battery Division
Post Office Box 28
Bloomfield, New Jersey 07003</td><td>1</td></tr>
<tr><td>Dr. A. J. Bard
University of Texas
Department of Chemistry
Austin, Texas 78712</td><td>1</td></tr>
<tr><td>Dr. F. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
Anaheim, California 92803</td><td>1</td></tr>
<tr><td>Dr. M. G. Sceats
University of Rochester
Department of Chemistry
Rochester, New York 14627</td><td>1</td></tr>
</table>

TECHNICAL REPORT DISTRIBUTION LIST, 359

No.
Copies

No.
Copies

Dr. Faul Delahay
New York University
Department of Chemistry
New York, New York 10003   1

Dr. R. A. Osteryoung
Colorado State University
Department of Chemistry
Fort Collins, Colorado 80521   1

Dr. E. Yeager
Case Western Reserve University
Department of Chemistry
Cleveland, Ohio 41106   1

Dr. D. N. Bennion
University of California
Chemical Engineering Department
Los Angeles, California 90024   1

Dr. R. A. Marcus
California Institute of Technology
Department of Chemistry
Pasadena, California 91125   1

Dr. J. J. Auborn
Bell Laboratories
Murray Hill, New Jersey 07974   1

Dr. Adam Heller
Bell Telephone Laboratories
Murrary Hill, New Jersey 07974   1

Dr. T. Katan
Lockheed Missiles & Space
  Co. Inc.
P.O. Box 504
Sunnyvale, California 94088   1

Dr. Joseph Singer, Code 302-1
NASA-Lewis
21000 Brookpark Road
Cleveland, Ohio 44135   1

Dr. L. Brummer
EIC Incorporated
Five Lee Street
Cambridge, Massachusetts 02139   1

Library
P. R. Mallory and Company, Inc.
Northwest Industrial Park
Burlington, Massachusetts 01803   1

Dr. P. J. Hendra
University of Southhampton
Department of Chemistry
Southhampton SO9 5NH
United Kingdom   1

Dr. Sam Perone
Purdue University
Department of Chemistry
West Lafayette, Indiana 47907   1

Dr. Royce W. Murray
University of North Carolina
Department of Chemistry
Chapel Hill, North Carolina 27514   1

Naval Ocean Systems Center
San Diego, California 92152
Attn: Technical Library   1

Dr. J. H. Ambrus
The Electrochemistry Branch
Materials Division, Research
  & Technology Department
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910   1

Dr. G. Goodman
Globe-Union Incorporated
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201   1

Dr. J. Boechler
Electrochimica Corporation
Attention: Technical Library
2485 Charleston Road
Mountain View, California 94040   1

Dr. P. P. Schmidt
Oakland University
Department of Chemistry
Rochester, Michigan 48063   1